



Project Summary

Separation of Dilute Hazardous Organics by Low Pressure Composite Membranes

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The use of membrane processes for waste purification and volume reduction is gaining considerable attention in many industries. For hazardous wastes containing priority organics and salts, reverse osmosis membranes can provide simultaneous separation of both organics and inorganics. The industrial development of non-cellulosic, (aromatic polyamide, sulfonated polysulfone, etc.) thin-film, composite membranes has provided a means for reverse osmosis treatment with high solute separations and minimal compaction problems.

The separation of dilute hazardous organics was accomplished through this project utilizing thin-film, composite, aromatic polyamide membranes. This technique offers advantages in terms of high solute separation at low pressures (1-2 MPa (145-290 psi)) and broad pH operating ranges (pH 2 to 12). The synthetic organic waste solutions used in this study include polyaromatic hydrocarbons (PAH), phenol, chlorophenols, nitrophenols, and chlorobenzenes. The actual organic waste solution was obtained from the site of a former wood treatment processing plant in Texas and was known to contain chlorophenols. The membrane showed excellent stability over long periods of time. Standard NaCl rejections were 97-99% and the average pure water flux at 2.068 MPa (300 psi) was about $14 \times 10^{-4} \text{ cm}^3/\text{cm}^2\text{s}$ ($5.5 \times 10^{-4} \text{ in}^3/\text{in}^2\text{S}$).

This Project Summary was developed by EPA's Hazardous Waste Engineering

Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Industries engaged in organic chemical manufacturing use contact process water, and the spent aqueous wastes often contain various hazardous priority pollutants. Of the 272-363 million metric tons (300 to 400 million short tons) of industrial solid wastes generated in the United States each year, it is estimated that 38 million metric tons (42 million short tons) are hazardous. Sixty-two percent of this waste is generated by the chemical products industry. Another source of aqueous hazardous waste is from unsecured industrial waste storage and from disposal site leachate. These contaminants are diverse in composition and concentration, and contain a broad spectrum of priority organics. Generally, the term hazardous or toxic organics includes synthetic organic compounds such as pesticides, herbicides, PCBs, and chlorinated hydrocarbons. Many contaminant streams are relatively dilute and thus a concentration step prior to detoxification or disposal may be necessary.

There are several techniques that have been used to treat dilute aqueous wastes. These include biological treatment, chemical coagulation, carbon adsorption, resin adsorption, stripping, and membrane processes. Using membrane processes for waste purification is gaining con-

siderable attention in many industries. Membrane transport mechanisms range from molecular diffusion in solids that are liquid-like to tortuous viscous flow through microporous polymers. The three major membrane processes for water and wastewater treatment are electrodialysis, reverse osmosis, and ultrafiltration. Reverse osmosis can remove salts, organics and ionic species. Ultrafiltration removes solute species primarily based on molecule sizes of 10-200 Å (3.9×10^{-8} - 7.9×10^{-7} inches). Electrodialysis separation is based on ionic charge of the solute. The reverse osmosis process separates solutes based on relative diffusivities of the solutes through the membrane (molecule size of 2-10 Å (7.9×10^{-9} - 3.9×10^{-8} inches)) at a given pressure differential.

Membrane Separation Concepts

Membrane processes are generally evaluated in terms of three parameters: membrane rejection (R), permeate-water flux (J_w), and extent of water recovery (r). The membrane rejection parameter, R, is a measure of the extent of solute separation,

$$R = 1 - \frac{C_p}{C_i} \quad (1)$$

in which C_p and C_i are the permeate and feed-stream solute concentrations, respectively. Primary separation of solutes occurs at the thin-film (skin) barrier layer. Thin-film membranes result in higher flux at pressures considerably less than asymmetric cellulose-acetate membranes.

A number of models have been developed to describe the transport of solute and solvent through membranes. A commonly used model is the solution-diffusion model. The water and solute fluxes (under a chemical-potential driving force) are given by:

$$\begin{aligned} \text{water, } J_w &= A(\Delta P - \Delta \pi) \text{ and;} & (2) \\ \text{solute, } J_s &= B(\Delta C); & (3) \end{aligned}$$

in which ($\Delta P - \Delta \pi$) is the net trans-membrane pressure, and "A" is the membrane permeability (function of temperature) constant. In Equation 3, "B" and "C" are solute permeability (function of solute-distribution coefficient between solution phase and membrane phase) and concentration gradient between the membrane surface and the permeate, respectively. In the case of negligible concentration polarization, ΔC and $\Delta \pi$ become the concentration and osmotic pressure difference between the bulk solution and the permeate, respectively.

Surface Force-Pore Flow

The model developed by Sourirajan gives a better understanding of the rejection and flux phenomena. The negative and positive adsorption of solute at the membrane-solution interface arises from net repulsive or attractive forces acting on the solute from the adjacent membrane surface. The model admits that a layer of water is preferentially adsorbed at the pore wall. In some cases this layer of water can be displaced by some molecules of solute exerting stronger adsorption forces toward the pore wall. For example, the Stoke's radius of water and phenol are 0.87 Å and 2.1 Å (3.4×10^{-9} - 8.3×10^{-9} inches), respectively. A layer of phenolics displacing the water layer will definitely cause a water flux drop by reducing the available path of the fluid. This phenomenon occurs at low pH under no ionization of the solutes.

In order to predict the separation of organics by a membrane, one needs to know the pore distribution of the membrane. The skin pore distribution of the membrane used in this study was measured by CO_2 (217°K) and by N_2 (77°K) gas adsorption technique. Utilizing the pore distribution, and a new calculation technique for the simultaneous solution of the radial velocity profile of the solvent through the pores, the solute concentration in the product water and the interaction parameters were applied to compute rejection of phenolics. Figure 1 shows excellent agreement between calculated and experimental results for a typical run involving nitrophenols.

Objectives

The development of a low pressure membrane (noncellulosic composite membranes) process to concentrate selected priority pollutants from hazardous wastes will substantially improve conventional destruction techniques. This work deals with the use of thin-film, composite membranes for concentration and separation of pollutants from aqueous waste streams. Spiked waste streams utilized included PAHs, phenolics, chloro- and nitrophenols, chlorinated benzenes, phthalates and heavy metals. An actual waste stream was also collected for treatment in the membrane system. Separation of pollutants and operation of the membrane system were evaluated as a function of system pressure, flow rate, and input waste concentration.

Experimental Procedure

Membrane studies were conducted in batch, continuous thin channel, and con-

tinuous spiral-wound modules (Figures 2 and 3). The batch operating conditions were 1400-1800 ml of feed solution, a system pressure (ΔP) of 1.38 - 2.07 MPa (200-300 psi) and pH = 4.5-11.8. The continuous operating conditions were ΔP = 0.69-2.07 MPa (100-300 psi) Reynold's number (Re) = 4000-9000, and pH = 3.3 - 11.8. For both the batch and continuous systems standard distilled water flux and salt (NaCl) rejection were obtained prior to experiments with any hazardous organic compounds. The membranes used in this study were made of aromatic polyamide. For each experimental run, samples of feed, concentrate, and permeate were collected, properly stored, and analyzed.

Membrane feed, concentrate, and permeate samples were analyzed in terms of total organic carbon (TOC) (direct injection), high performance liquid chromatography (HPLC) (direct injection or after solvent extraction if below detection limit), and gas chromatography (GC) (after solvent extraction-concentration). The reproducibility and recovery of the solvent extraction-concentration step were checked with known synthetic solutions and spiked samples. The objectives of the HPLC analysis by reverse phase columns were two-fold: establishment of membrane output concentrations and correlation of membrane rejection behavior with HPLC elution times. Previous studies have indicated an increase in rejection with HPLC elution time.

Results

Membrane separation (batch cell and continuous unit) of selected classes of priority pollutant mixtures was studied at 0.69 - 2.07 MPa (100 to 300 psi). The batch cell study focused on the mixtures of selected sparingly soluble PAH compounds (naphthalene, anthracene, phenanthrene), phenols, phthalates, chlorobenzenes, and a field-collected, contaminated ground-water sample. The continuous unit study focused on the mixtures of selected chlorophenols and nitrophenols. One run involving phenol and a salt mixture was also conducted. For chloro- and nitro-phenols, a wide range of pH values was selected to establish the rejection behavior of nonionized and ionized species. Membrane stability for both the continuous and batch units was checked with standard NaCl runs and with distilled water. The membrane shows a 15% drop in distilled water flux with standard NaCl rejections remaining constant at 97-98%, indicating good membrane stability.

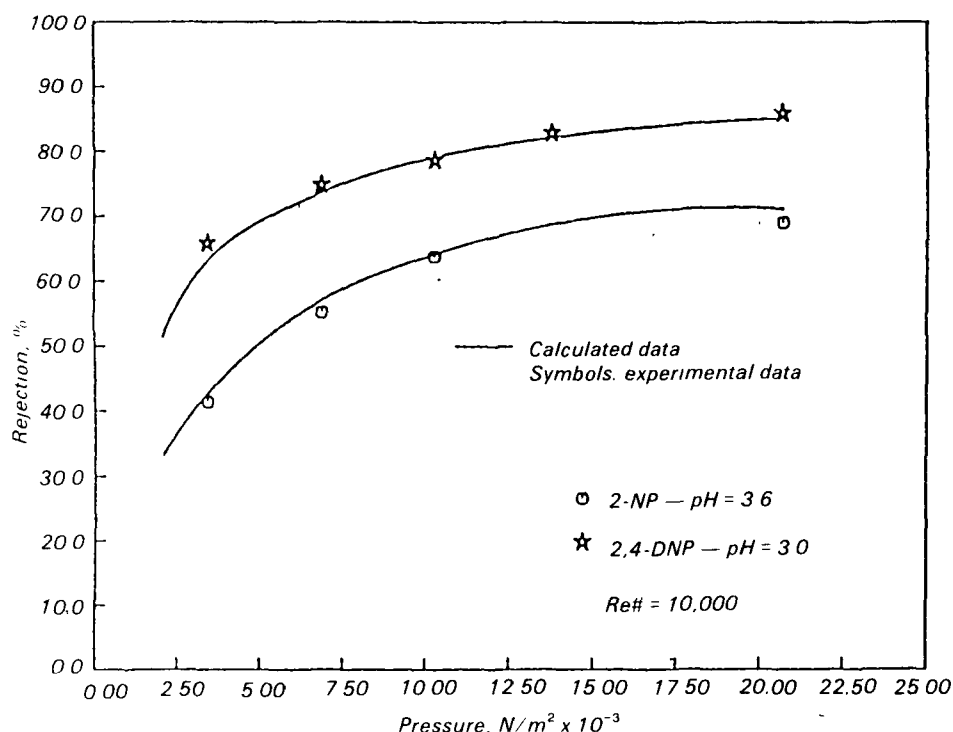


Figure 1. Effect of pressure on experimental and calculated rejections of single solutions of 2-NP, 2,4-DNP

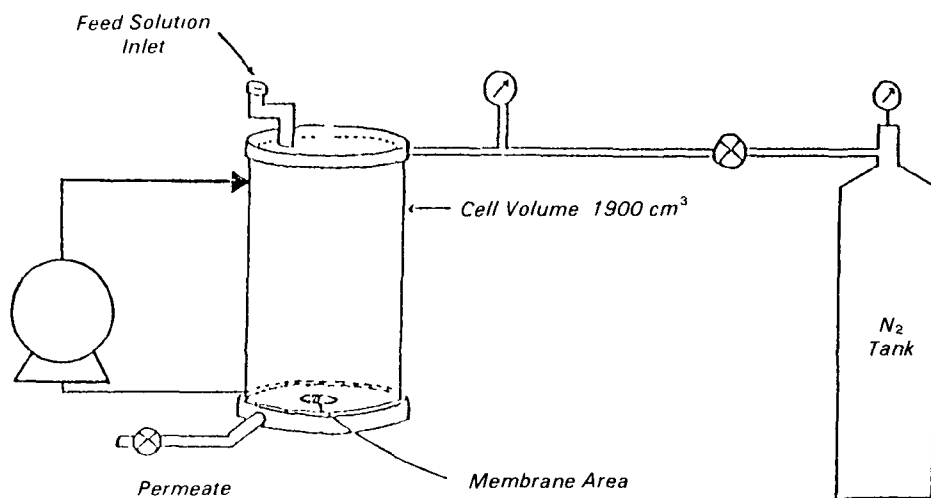


Figure 2 Batch membrane unit

Separation of naphthalene (solubility 20-22 mg/l), anthracene (solubility 0.12 mg/l), phenanthrene (solubility 0.58 mg/l), and dimethylphthalate (solubility 278 mg/l) was carried out in the batch cell. Rejection of dimethylphthalate was

about 97%, and rejection of naphthalene was 98.0%. For the higher molecular weight anthracene and phenanthrene, which are chemically similar to naphthalene, the rejections were 98-99%. The flux drops with these compounds were

only 3-5%. The material balance analysis of PAH compounds showed significant loss of these compounds through the test, probably due to adsorption on the membrane.

Additional experimental runs were performed on a mixture of chlorophenols (phenol, 2-chlorophenol (2-CP), 2,4-dichlorophenol (2,4-DCP), 2,4,6-trichlorophenol (2,4,6-TCP), and 4-chlorocresol (4-CCR)), and nitrophenols (2-nitrophenol (2-NP) and 4-nitrophenol (4-NP)). It is important to emphasize at this point that phenolics are ionizable species. As such, the pH values of various mixtures were varied from pH = 4.5 to pH = 11.8 to observe the separation characteristics at various ionization conditions. At solution pH > 11 essentially all species are 100% ionized.

Experimental runs involving the chlorophenol mixture were performed at pH values of 5, 9, and 11. In each chlorophenol experimental run involving high pH, there was a smaller drop in permeate flux than in low-pH runs. The rejection of the individual species increases with pH value and with each chloro substitution on the phenol molecule. Similar runs with nitrophenol mixtures at high pH (pH = 11.5) showed very high rejections of phenol (98.3%), 2-NP (99.3%), and 4-NP (99.1%).

The chlorinated benzenes were run in the batch cell as a mixture of chlorobenzene (CB), 1,4-dichlorobenzene (1,4-DB, and 1,2,4-trichlorobenzene (1,2,4-TCB). Similar mixtures were tested under stirred and quiescent conditions. Both tests were taken to at least 80% recovery of the feed solution and both showed rejections ranging from 67.6 to 99.7%.

Experiments with contaminated water from a wood processing plant were conducted in the batch reactor at pH 7 and at pH 11. The various phenol and PAH compounds in the wastewater performed quite similarly to the compounds tested in the synthetic waste mixtures. Total rejection of organics in the waste stream ranged from 87% to 97%.

Continuous runs were made with chloro- and nitro-phenol mixtures in the turbulent flow regime. High flux drop was observed under non-ionization conditions (pH = 3.3) of the various solutes. These results were obtained even under a high Reynolds number (9000). The behavior was similar to that observed in the batch cell.

To establish the flux drop and rejection phenomena, various types of mixtures were run using thin channel cells. Runs

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The complete report, entitled "Separation of Dilute Hazardous Organics by Low Pressure Composite Membranes," (Order No. PB 87-214 870/AS; Cost: \$18.95, subject to change) will be available only from:

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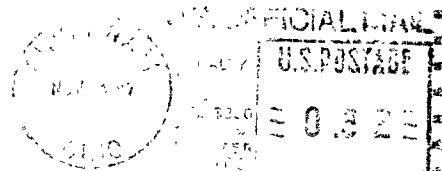
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